Electrochemical evaluation of manganese reducers – Recovery of Mn from Zn–Mn and Zn–C battery waste

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HIGHLIGHTS

- The reduction reaction of MnO_2 to Mn^{2+} was studied.
- The analysis of oxidation-reduction potentials for specific reducers was carried out.
- It was found that the best results of leaching were obtained by the use of oxalic acid as the reducer.

ARTICLE INFO

ABSTRACT

Extraction of manganese from ores or battery waste involves the use of reductive reagents for transformation of MnO_2 to Mn^{2+} ions. There are many reducers, both organic and inorganic, described in the literature. A series of 18 reducers has been discussed in the paper and they were classified according to standard redox potential ($pE = -\log a_{e-}$ where pE is used to express formal electron activity and a_{e-} is formal electron activity). The experiments of manganese extraction from paramagnetic fraction of Zn–C and Zn–Mn battery waste in the laboratory scale have been described for 3 reducers of different origin. The best result was achieved with oxalic acid (75%, with the lowest redox potential) and urea (with typical redox potential) appeared inactive. Extraction supported by hydrogen peroxide resulted in moderate yield (50%). It shows that formal thermodynamic scale is only preliminary information useful for selection of possible reducers for manganese extraction resources.

1. Introduction

Both in the case of natural manganese resources (ore) and waste sources (batteries), the basic condition of activation of this element and extraction it to the solution is the change of the oxidisation level to 2+ (which is specific to $MnSO_4$) and the most problematic is the change from the 4 + oxidation level (which is specific for MnO_2). This requires the application of a reducer which is efficient in a highly acidic environment of the leaching solution.

Batteries waste, depending on the type, contain various heavy and toxic metals being dangerous for soil and groundwater. Most types of batteries can be recycled based on pyro- and hydrometallurgical processes [1]. According to a review of literature, non-

ferrous metal ions (including Zn(II)) can be effectively separated and removed from aqueous solution in ions flotation, liquid–liquid extraction, or transport across liquid membrane processes [2–6].

2. Manganese ores

2.1. Non-organic reducers

According to the literature one of the most studied non-organic reducer for manganese ores is hydrogen peroxide (30% solution of H_2O_2). The work of Jiang et al. [7] presents the test results of the continuous manganese and silver leaching with the application of sulphuric acid and the addition of hydrogen peroxide. The obtained results corresponded to 98% output of manganese and 85% output of silver.

Literature provides a great number of studies on the simultaneous leaching of oxide manganese ores and sulphide minerals (which at the same time functioned as reducing factors). Sulphuric

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(H$_2$SO$_4$) or hydrochloric (HCl) acid were used in this process, the following minerals were tested: galena (PbS) [8], sphalerite (ZnS) [8–10], pyrite (FeS$_2$) [8], [11–14], nickel ores [15] and pyrite lignite [16]. In the majority of works, authors obtained a level of over 90% for manganese leaching from ores and sludge containing manganese in the amount both under and over 40% of the weights. Another non-organic reducer which could be applied in order to increase the level of recovery of Mn from manganese ores is hydrazine [17]. The application of acid solutions of iron(II) ions for leaching of poor ores and industry wastes was described in the works of Brantley et al. [18], Das et al. [19] and Vu et al. [20].

2.2. Organic reducers

The review of literature allows for the assumption that some organic substances can function as efficient reducers for manganese(IV) oxide contained in ores [21]. These substances include: glucose and sucrose [22,23], cellulose [24], lactose [25,26], glycerol [27], alcohols (MeOH, EtOH, n-BuOH, i-PrOH) [28], thiourea [29] and organic weak acids such as oxalic acid [30].

The literature also provides examples of studies on bio-reducing leaching of manganese oxides. The authors of several works [31,32] indicate the potential application of autotrophic microorganisms for reduction of leaching from ores containing manganese oxides. Chemolithotrophic microbes use non-organic compounds as an energy source, and simultaneously a large amount of organic acids (citric, oxalic acid) is created during their metabolism [33,34]. The acids can contain the MnO$_2$ reducer.

3. Zn–C and Zn–Mn (alkali) battery wastes

3.1. Characteristics of zinc–carbon (Zn–C) and zinc–manganese (Zn–Mn) batteries

Electrochemical energy sources − that are currently applied − can be divided into three basic groups: (1) the first type cells (so called primary, irreversibly utilising the electrochemical process), (2) the second type (often referred to as reversible due to application of reversible electrochemical processes, otherwise known as accumulators), and (3) fuel cells (burning fuels in electrochemical reactions).

The first type of cells primarily includes the most popular today zinc–carbon and zinc–manganese (alkali) batteries [36]. The structure of these cells and their overall material and elemental composition were developed long ago. The first prototype was the Leclanché's cell. It was composed of a zinc anode and cathode from manganese dioxide, formed with the addition of graphite, immersed in ammonium chloride solution. At the beginning of the nineteenth century it was modified by replacing the liquid electrolyte with a paste from partially dehydrated gypsum and ammonium chloride, with the addition of zinc chloride. In a so called "dry" carbon–zinc cell, the positive electrode (cathode) is a graphite rod surrounded with a mixture of manganese oxide (MnO$_2$) and powdered graphite whereas the negative electrode (anode) is a zinc cup, acting simultaneously as a container. The electrolyte is a water solution of starch saturated with ammonium chloride (NH$_4$Cl) and zinc chloride (ZnCl$_2$), separated from the cathode with a paper spacer. Due to corrosion of the zinc container and possibility of "spilling" of the aggressive electrolyte, the cells can be very dangerous for the electronic equipment. The anode material in an alkali zinc–manganese cell is zinc powder in a gel matrix (e.g. starch or poly-acrylic acid gel). The cathode material is manganese dioxide (MnO$_2$), mixed with carbon (graphite or carbon black), obtained by electrochemical processes. The cell is enclosed in a steel container, acting simultaneously as the cathode power collector. The electrolyte is a

concentrated solution of potassium hydroxide (KOH). To prevent from corrosion of metallic zinc (which is the anode material) zinc oxide was added. In some cases, electrolyte in the form of a gel is used. Solution of potassium hydroxide guarantees a high ion movement in a wide range of temperature in which the cells may be used. For zinc–manganese cells, the following electrode reactions can be proposed: (anode) Zn = Zn^{2+} + 2e$^-$ and (cathode) 2MnO$_2$ + 2H$_2$O + 2e$^-$ = 2MnO(OH) + 2OH$^-$.

3.2. Battery waste processing

Currently, there are three methods of spent battery processing, i.e.: separative (mechanical), pyrometallurgical and hydrometallurgical (both chemical in the origin). The separative (mechanical) methods are frequently used for large batteries (industrial type) and as preliminary operations in other processing technologies. They consist in mechanical loosening of the structure (body) of the battery and separation of components of characteristic physical properties (i.e. density, size, magnetic properties). These operations are easier and cheaper than other processes, and thus, are used for the preparation of the material stream for further chemical processing.

Pyrometallurgical methods are based on material recovery (metals in particular) by their alteration in adequately high temperatures into specific condensed phases (including metallic alloys) or into gas phase with latter condensation. Generally, these methods are suitable for phases rich with recovered components or concentrated in higher temperatures in the gas phase (this relates to e.g. removal of mercury, acquisition of cadmium or zinc). In terms of batteries, these processes can also be performed in a traditional way, i.e. by oxidising–reducing equilibrium of the HCO (hydrogen, carbon, oxygen) system, as well as in a broad manner, which is appropriate for advanced chemical metallurgy, e.g. when chlorination processes are used. However, it is important to remember that this classification is conventional and is not appropriate for precise chemical or technological considerations. The advantage of pyrometallurgical methods is the possibility to recycle various types of cells (batteries), including also cells containing various organic materials.

Hydrometallurgical methods are frequently based on acidic or alkaline leaching of appropriately prepared battery wastes (after phases of mechanical processing). It is followed by a series of physical and chemical operations that leads to the separation and concentration of valuable or troublesome components between appropriate phases and gives commercial products or intermediates for separate technological processes (pyrometallurgical or hydrometallurgical) or wastes. Generally, hydrometallurgical processes are less energy-consuming than pyrometallurgical ones, however the waste generated in these processes are more troublesome. The advantage of hydrometallurgical processes is that they allow simultaneous processing of mixtures of various types of batteries Table 1.

Table 1
Typical composition of zinc–carbon and zinc–manganese batteries, in wt. % [35].

Component	Input, wt. %		
	Zn–C, type D	Zn–C, type A	Zn–Mn, type D
Paper	0.96–2.24	3.21–5.80	1.15
Steel	18.30–24.06	30.48–35.79	11.66
Plastic	2.11–3.08	2.66–2.87	1.27
Graphite rod	4.54–6.12	5.85–6.86	–
Powder	52.47–64.46	46.33–49.19	40.76
Water (moisture)	5.80–13.91	1.50–4.93	2.71
Black paste	–	–	41.81
Other	0.34–1.28	1.24–3.31	0.64

3.3. Fine fraction of stream of spent zinc–carbon (Zn–C) and/or zinc–manganese (Zn–Mn) batteries – manganese resource
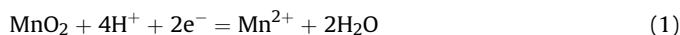
In case of the stream of spent zinc–carbon (Zn–C) and/or zinc–manganese (Zn–Mn) batteries, the first phase of the recycling process is the mechanical processing (provided that the next phase of the processing is the hydrometallurgical method). This operation results in the fine fraction – referred to as battery powder (battery "black mass") – that mainly contains metals (manganese, zinc) and graphite as well as a fraction of larger grains composed of "scrap iron", plastics, paper and binding agents. The hydrometallurgical processing is only performed on the battery "black mass". Some examples of typical composition of battery "black mass" is presented in Tables 2 and 3. Obtaining high levels of transition of manganese to a solution during the acidic leaching of the battery resource is hindered due to a high presence of manganese dioxide (MnO_2) – Table 3 (manganese at 4 + oxidisation state is the most stable) [37]. Therefore, the selection of an appropriate reducer and conditions of acidic leaching are important for the efficiency of the process.

According to the literature, hydrogen peroxide was the most frequently used as a reducer of manganese dioxide for the battery "black mass" from spent Zn–C and Zn–Mn batteries [39], [42], [46–49]. Sayilgan E. et al. [36], Ferella F. et al. [38] and de Michelis I. et al. [50] performed trials with the use of simple organic acids ($C_6H_8O_6$, $C_6H_8O_7$, $C_2H_2O_4$) whereas Avraamides J. et al. [51] and Furlani G. et al. [52] used lactose as a reducer ($C_{12}H_{22}O_{11}$). In the work of Senanayake G. et al. [43] and Ferella F. et al. [44], for reduction of Mn(IV), gaseous SO_2 was used. With reference to these studies the parameters of acidic leaching and used reducers were collected in Table 4.

4. Oxidation-reduction potential – MnO_2 reducers sequence

4.1. Reduction of MnO_2 to Mn^{2+}

The desirable reaction of reduction in the considered system is:

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O \qquad (1)$$

For this reaction the equilibrium constant is (a_e – formal electron activity):

$$K = \frac{a_{Mn^{2+}}}{a_{MnO_2} \cdot a_{H^+}^4 \cdot a_{e^-}^2} \qquad (2)$$

and:

$$\lg K = -4\log a_{H^+} - 2\log a_{e^-} + \log \frac{a_{Mn^{2+}}}{a_{MnO_2}} \qquad (3)$$

which is equivalent to:

$$\lg K = 4pH + 2pE + \log \frac{a_{Mn^{2+}}}{a_{MnO_2}} \qquad (4)$$

Which after conversion shall have the form (for $n = 2$):

$$pE = pE^0 - \frac{4}{2}pH - \frac{1}{2}\log \frac{a_{Mn^{2+}}}{a_{MnO_2}} \qquad (5)$$

The temperature dependence of parameter pE^0 is calculated with use of the HSC Chemistry® for Windows, ver. 5.1, Outotec Oy, Finland. Its values, including other thermodynamic parameters, are presented in Table 5.

4.2. Reducers associated with MnO_2/Mn^{2+} reaction

Examples of manganese reduction to a solution from ores as well as battery waste with the use of various reducers were provided in the previous sections. Calculation of the oxidation-reduction potential of substances used for this purpose allows their systematisation and thermodynamic evaluation of the reductive capacity in relation to MnO_2/Mn^{2+} reaction. For this purpose, 18 chemical species (reducers) were selected. These species were characterised by standard red-ox potential and compared with MnO_2/Mn^{2+} reaction potential (presented in Table 6). The first verse of the table presents the basic reaction, i.e. reaction of reduction in an acidic environment of solid manganese(IV) oxide to manganese(II) ion in the solution. The pE dependence corresponding to this reaction was specified earlier as Eq. (5) whereas the equation in Table 6 includes the activity of the solid MnO_2 as a pure phase ($a_{MnO2} = 1$). The pE^0 values (of oxidation-reduction potential for the standard state) were calculated for three various temperatures, taking into account the leaching conditions, frequently performed in higher temperatures. The verse 2 (No.2)

Table 2
Comparison of elemental composition of various battery powders from spent zinc–carbon (Zn–C) and/or zinc–manganese (Zn–Mn) batteries, in g kg^{-1} presented in the literature.

Source	Ferella F. et al. [38]	Veloso L.R.S. et al. [39]	Salgoda A.L. et al. [40]	de Souza C.C.B.M et al. [41]	de Souza C.C.B.M et al. [42]	Senanayake G. et al. [43]
Metals	a^*	b^*	b	b	b	b
Mn	33.6	36.5	31.1	45.0	44.0	22.7
Zn	14.5	17.0	19.6	21.0	20.6	20.8
Fe	0.50	0.07	0.17	0.36	0.49	2.65
Cr	0.19	–	–	–	–	
Al	0.36	–	–	–	–	0.28
K	3.26	4.53	7.25	4.70	4.90	0.4
Cl	3.38	–	–	–	–	2.25
Ti	0.27	–	–	–	–	0.66
Si	0.49	–	–	–	–	0.29
Na	–	0.13	0.10	–	–	0.07
Hg	–	<0.002	0.015	0.001	0.001	0.02
Pb	–	–	0.005	0.03	0.06	0.07
Ni	–	–	$\sum$ 0.03	–	–	0.04
Cd	–	–		0.00006	0.000006	
Co	–	–		–	–	0.01
S						0.16
Cu						0.04
Ca						0.06
Mg						0.02

*a – battery powder from zinc–manganese (Zn–Mn) and zinc–carbon (Zn–C) batteries.
*b – battery powder from zinc–manganese (Zn–Mn) batteries.

Table 3
Speciation of Zn, Mn and K in spent batteries on the basis of x-ray scattering analysis (iron only as Fe_2O_3, carbon in the form of graphite).

Authors	Type of battery	Zn	Mn	K
de Souza C.C.B.M et al. [41]	Zn–Mn (not washed off)	ZnO	Mn_2O_3 Mn_3O_4 MnO_2	–
de Souza C.C.B.M et al. [42]	Zn–Mn (not washed off)	ZnO	Mn_2O_3 Mn_3O_4 MnO_2	–
Ferella F. et al. [43]	Zn–Mn	ZnO	MnO_2 Mn_3O_4	KOH
	Zn–C (not washed off)	$Zn_5(OH)_8Cl_2 \cdot H_2O$		
	Zn–Mn Zn–C (washed off)	ZnO	Mn_3O_4 Mn_2O_3 MnO_2	–
Li Y. et al., [45]	Zn–Mn (not washed off)	$[Zn(OH)_2]_4 \cdot Zn-Cl_2$ $ZnMn_2O_4$ $Zn(NH_3)_2Cl_2$	$Mn(OH)_2$ Mn_2O_4 γ-Mn_2O_2 $ZnMn_2O_4$ $Zn(NH_3)_2Cl_2$	–

Table 4
Parameters of acidic leaching of Zn–C and Zn–Mn battery resources with the addition of MnO_2 reducer, s/l − proportions of the solid phase and the solution.

Authors	Reducer	Resource	Process conditions	Recovery
Kim T-H. et al. [47]	H_2O_2	Zn–C	2 M H_2SO_4, $T = 60$ °C, $t = 1$ h, s/l = 1/10	Zn 98.0%, Mn 97.9% Fe 55.2%
Shim S-M. et al. [49]	H_2O_2	Zn–C	2 M H_2SO_4, $T = 60$ °C, $t = 1$ h, s/l = 1/10	Zn 93.3%, Mn 82.2%
Bartolozzi M. et al. [46]	H_2O_2	Zn–Mn	6 M H_2SO_4, $T = 50$ °C, $t = 2$ h, s/l = 1/5	Mn 55%, Ni, Cd, Hg 75% Zn, Fe 100%
de Souza C.C.B.M. et al. [42]	H_2O_2	Zn–Mn	0.13 M H_2SO_4, $T = 50$ °C, $t = 2$ h, s/l = 1/50	Zn 100%, Mn 30%
Veloso L.R.S. et al. [39]	Washing off	Zn–Mn	H_2O, T = 25 °C, $t = 0.33$ h, s/l = 1/5	K 99%
	H_2O_2		0.56 M H_2SO_4, $T = 40$ °C, $t = 0.33$ h, s/l = 1/30	Zn, Mn 100%
de Michelis I. et al. [50]	$C_2H_2O_4$	Zn–C Zn–Mn	1.8 M H_2SO_4, 59.4 g dm^{-3} $C_2H_2O_4$, $T = 80$ °C, $t = 5$ h	Zn 100%, Mn 70%
Avraamides J. et al. [51]	$C_{12}H_{22}O_{11}$	Zn–C Zn–Mn	2 M H_2SO_4, 5 g dm^{-3} $C_{12}H_{22}O_{11}$, $T = 70$ °C, s/l = 1/10, $t = 4$ h	Zn 100%, Mn 100%
Furlani G. et al. [52]	$C_{12}H_{22}O_{11}$	Zn–C Zn–Mn	2 M H_2SO_4, 9 g dm^{-3} $C_{12}H_{22}O_{11}$, $T = 90$ °C, s/l = 1/10, $t = 3$ h	Zn 98%, Mn 100%
Senanayake G. et al. [43]	SO_2 (gas)	Zn–C Zn–Mn	1 M H_2SO_4, 50 ml min^{-1} SO_2, $T = 30$–40 °C, s/l = 1/10, $t = 1.5$ h	Zn 98 ± 2%, Mn 98 ± 2% Fe 25 ± 2%
Ferella F. et al. [44]	SO_2 (gas)	Zn–C Zn–Mn	0.1 M H_2SO_4, 200 ml min^{-1} SO_2, $T = 30$ °C, s/l = 1/10, $t = 0.25$ h	Zn 99%, Mn 99%

Table 5
Temperature dependence of the standard free enthalpy, equilibrium constant and potential vs. hydrogen electrode (compatible parameters) for reaction $MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$.

Temperature °C	ΔG_r^0 kJ	K	$E^{\#)}$ V	pE^0
15	−238.4	$1.65 * 10^{43}$	1.236	21.62
25	−237.2	$3.64 * 10^{41}$	1.230	20.79
35	−236.0	$1.03 * 10^{40}$	1.224	20.02
45	−234.9	$3.70 * 10^{38}$	1.218	19.30
55	−233.8	$1.63 * 10^{37}$	1.212	18.62
65	−232.6	$8.71 * 10^{35}$	1.206	17.98
75	−231.5	$5.53 * 10^{34}$	1.201	17.38
85	−230.5	$4.11 * 10^{33}$	1.195	16.82
95	−229.4	$3.54 * 10^{32}$	1.190	16.28

of Table 6 includes data for the $Cl_2(g)/Cl^-$ reaction. Under standard conditions the chloride ion cannot act as the manganese(IV) reducer, however the potentials of both reactions can become equal, especially in high temperatures, highly acidic environments, with high concentrations of chloride ions, low concentrations of manganese(II) and removal of chlorine gas from the system. Furthermore, the Mn^{2+} ions can form $MnCl^+$ cation complexes according to the $Mn^{2+} + Cl^- = MnCl^+$ reaction, the equilibrium constant of which increases from approximately 2 at the temperature of 25 °C to approximately 10 at 85 °C. Therefore, it is possible

to consider the MnO_2 reduction to a complex form: $MnO_2 + 4H^+ + Cl^- + 2e^- = MnCl^+ + 2H_2O$. However, the pE^0 values of the basic reaction taking into account the complex do not change significantly, the increase is only by 0.2−0.5 units in comparison with the data in Table 6 (to 20.94 at 25 °C, 18.94 at 55 °C and 17.33 at 85 °C, respectively). The outcome of two forms of manganese ions ($MnCl^+$ and Mn^{2+}) is in simple relation with the equilibrium constant of complexing reaction. Therefore, it is necessary to assume that the chloride ions can be taken into account as a reducer of manganese(IV) oxide to manganese(II) ion in the solution.

pE^0 oxidation-reduction potentials (in the standard state) of other reducers are significantly lower than the potential of the basic reaction. Relatively high in the sequence of potentials is the pair Fe^{2+}/Fe^{3+} (No. 3) and frequently used hydrogen peroxide (No. 4). The second reagent was the most frequently used in the processes of leaching for both manganese ores and battery waste (what was mentioned above). Iron ions are also included in the next group of reducers together with combination of sulphur and metal sulphides. These are specified in the verses 5−9 of Table 6. The $S_4O_3^{2-}$ ion (No. 5) is the only one given as an example from much broader group of ionic sulphuric reducers (SO_2, $S_2O_3^{2-}$, $S_2O_4^{2-}$, SO_3^{2-} or $S_2O_6^{2-}$) that may be also used as reducers. From the point of view of thermodynamic calculations the $S_4O_3^{2-}$ ion is dominating, that the equilibrium constants of disproportioning reactions of other ions to $S_4O_3^{2-}$ and SO_4^{2-} (for example $10SO_3^{2-} + 6H^+ = S_4O_3^{2-} + 6SO_4^{2-} + 3H_2O$ and

Table 6
pE0 − standard oxidation-reduction potentials of selected reducers for the acidic leaching of manganese materials (calculated with the HSC Chemistry® for Windows). (a) − species in the solution (reference state), (s) − solid phase, (g) − gaseous phase.

No.	Reducer	Red/ox reduction	pE equation	pE^0 25 °C	pE^0 55 °C	pE^0 85 °C
1	Basic reaction $MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$		$pE = pE^0 - 4/2pH - 1/2\log a_{Mn^{2+}}/a_{MnO_2}$	20.79	18.62	16.82
2	Cl^-	$Cl_2(g) + 2e^- = 2Cl^-$	$pE = pE^0 - 1/2\log a_{Cl^-}^2/p_{Cl_2}$	23.01	20.30	17.99
3	Fe^{2+}	$Fe^{3+} + e^- = Fe^{2+}$	$pE = pE^0 - \log(a_{Fe^{2+}}/a_{Fe^{3+}})$	13.03	12.36	11.80
4	H_2O_2	$O_2(g) + 2H^+ + 2e^- = H_2O_2(a)$	$pE = pE^0 - pH - 1/2\log(a_{H_2O_2})$	11.75	10.20	8.93
5*	$S_4O_3^{2-}$	$SO_4^{2-} + 26 H^+ + 20e^- = S_4O_3^{2-} + 13H_2O$	$pE = pE^0 - 13/10pH + 1/20\log(a_{S_4O_3^{2-}}/a_{SO_4^{2-}}^4)$	9.32	8.40	7.67
6	FeS_2	$Fe^{3+} + SO_4^{2-} + 16H^+ + 15e^- = FeS_2 + 8H_2O$	$pE = pE^0 - 16/15pH + 1/15\log(a_{Fe^{3+}} \cdot a_{SO_4^{2-}})$	7.02	6.99	6.99
7	PbS(s)	$Pb^{2+} + SO_4^{2-} + 8H^+ + 8e^- = PbS + 4H_2O$	$pE = pE^0 - pH + 1/8\log(a_{Pb^{2+}} \cdot a_{SO_4^{2-}})$	6.06	5.41	4.89
8	ZnS(s)	$Zn^{2+} + SO_4^{2-} + 8H^+ + 8e^- = ZnS + 4H_2O$	$pE = pE^0 - pH + 1/8\log(a_{Zn^{2+}} \cdot a_{SO_4^{2-}})$	5.60	5.04	4.61
9	NiS(s)	$Ni^{2+} + SO_4^{2-} + 8H^+ + 8e^- = NiS + 4H_2O$	$pE = pE^0 - pH + 1/8\log(a_{Ni^{2+}} \cdot a_{SO_4^{2-}})$	5.34	4.82	4.41
10	Thiourea CH_4N_2S	$N_2 + SO_2 + CO_2 + 12H^+ + 12e^- = CH_4N_2S + 4H_2O$	$pE = pE^0 - pH - 1/12\log(a_{CH_4N_2S}) - 0,120$	3.39	2.66	2.07
11	Adipic acid $C_6H_{10}O_4$	$6CO_2 + 26H^+ + 26e^- = C_6H_{10}O_4 + 8H_2O$	$pE = pE^0 - pH - 1/26\log(a_{C_6H_{10}O_4})$	1.69	1.13	0.666
12	Glutaric acid $C_5H_8O_4$	$5CO_2 + 20H^+ + 20e^- = C_5H_8O_4 + 6H_2O$	$pE = pE^0 - pH - 1/20\log(a_{C_5H_8O_4})$	1.53	0.970	0.507
13	Succinic acid $C_4H_6O_4$	$4CO_2 + 14H^+ + 14e^- = C_4H_6O_4 + 4H_2O$	$pE = pE^0 - pH - 1/14\log(a_{C_4H_6O_4})$	1.45	0.864	0.382
14	Urea $CO(NH_2)_2$	$N_2(g) + CO_2(g) + 6H^+ + 6e^- = CO(NH_2)_2(a) + H_2O$	$pE = pE^0 - pH - 1/6\log(a_{CO(NH_2)_2}) - 0,100$	1.36	0.794	0.326
15	Methanol CH_3OH	$CO_2 + 6H^+ + 6e^- = CH_3OH(a) + 3H_2O$	$pE = pE^0 - pH - 1/6\log(a_{CH_3OH})$	0.526	0.161	−0.136
16	Glycerol $C_3H_8O_3$	$3CO_2 + 14H^+ + 14e^- = C_3H_8O_3 + 3H_2O$	$pE = pE^0 - pH - 1/14\log(a_{C_3H_8O_3})$	−0.011	−0.410	−0.737
17	Glucose $C_6H_{12}O_6$	$6CO_2 + 24H^+ + 24e^- = C_6H_{12}O_6 + 6H_2O$	$pE = pE^0 - pH - 1/24\log(a_{C_6H_{12}O_6})$	−0.200	−0.610	−0.945
18	Hydrazine N_2H_4	$N_2(g) + 4H^+ + 4e^- = N_2H_4(a)$	$pE = pE^0 - pH - 1/4\log(a_{N_2H_4})$	−5.62	−5.49	−5.38
19	Oxalic acid $H_2C_2O_4$	$2CO_2(g) + 2H^+ + 2e^- = H_2C_2O_4(a)$	$pE = pE^0 - pH - 1/2\log(a_{H_2C_2O_4})$	−10.05	−10.37	−10.65

$10S_2O_4^{2-} + H_2O = 3S_4O_3^{2-} + 8SO_4^{2-} + 2H^+$) are heavily shifted to the right. As a consequence, the reaction specified in the verse 5 of Table 6 is characterised by the highest oxidation-reduction potential amongst the species formed by sulphur and oxygen. The next verses (No. 6–9) include examples of metal sulphides in the sequence of descending oxidation-reduction potentials. As mentioned above, such sulphides were used as reducers in processes of leaching of manganese ores. It is worth to note that these potentials are significantly higher than the one for the $SO_4^{2-} + 8H^+ + 8e^- = S^{2-} + 4H_2O$ reaction (sulphide ion, S^{2-}, as the reducer), and are equal in temperatures of 25, 55 and 85 °C, 2.59, 2.42 and 2.27, respectively.

The reduction potential of the sulphide ion is comparable (in the standard conditions) with the potential of thiourea (No. 10 in Table 6), however the temperature dependence of potential of the second substance is significantly stronger. The thiourea belongs to the group of reducers dominated by organic combinations. Their potentials are low, generally close to zero, while assuming full oxidisation to carbon dioxide (and, if it is necessary, to nitrogen and sulphur dioxide). Organic acids specified in the verses 11–13 are components of one of mixtures used in research [17] whereas substances in the verses 15–17 are examples of species with the hydroxyl (−OH) group. A short comment is required for carbamide, the oxidation-reduction potential of which is specified in the verse 14 of Table 6, for a direct reaction to nitrogen and carbon dioxide. Taking into account the thermodynamic data (HSC Chemistry® for Windows) for the reaction $CO_3^{2-} + 2NH_4^+ = 2H_2O + CO(NH_2)_2(a)$ (a − for the reference state in solution) the equilibrium constant of this reaction equals to 33 at the temperature of 25 °C, only 4.2 at 55 °C and 0.53 at 85 °C. After hydrolysis only ammonium ions can take part in the reduction. The oxidation-reduction potential of $N_2 + 8H^+ + 6e^- = 2NH_4^+$ reaction at temperatures of 25/55/85 °C equals to 4.6/4.3/4.0, respectively. However, if we consider that the ammonium ions may be combined into a complex with zinc (the main metal accompanying manganese in the processing of battery wastes), the reduction reaction shall take the form of $2N_2 + 12H^+ + 12e^- + Zn^{2+} = Zn(NH_3)_4^{2+}$ and the standard oxidation-reduction potential at temperatures of 25/55/85 °C equals to 2.3/1.9/1.6, respectively. In each of those cases the reduction of MnO_2 do Mn^{2+} is justified thermo-dynamically.

Table 6 also enlists two other substances: hydrazine (the verse No. 18) and oxalic acid (the verse No. 19). As mentioned above, both were used as reducers in the processes of manganese leaching. The oxidation-reduction potential of these substances in standard conditions is significantly lower, especially for the oxalic acid. Graphical comparison of reducers is presented in Fig. 1. From the point of view of thermodynamics, advantageous reducers are hydrazine and oxalic acid, chloride ions do not reduce MnO_2 (in specified conditions), and the rest of chemical species (reducers) would be in the middle of considered pE scale.

5. Extraction of manganese from waste of batteries

5.1. Materials

The studied material − paramagnetic fraction, was delivered by one of the Polish (Lower Silesia) companies which purchases and recycles small size batteries and accumulators, collects and processes spent electric and electronic equipment, and also collects and neutralises hazardous waste.

Spent batteries are supplied mainly by large recovery organisations operating in Poland and via private collection system. Battery waste is sorted manually on a conveyor and is subject to generic segregation. Items that do not undergo recycling (electric fences for farm animals, mercury batteries, nickel-hydride
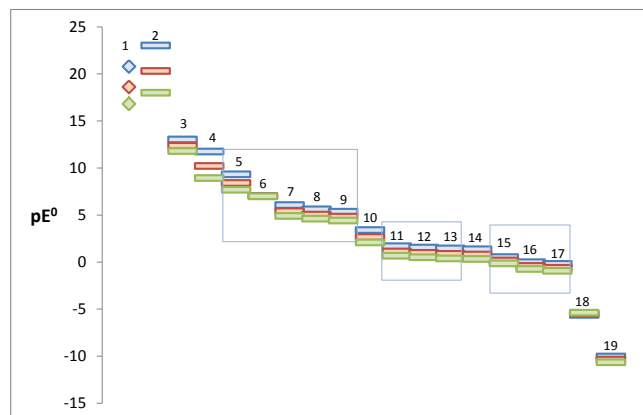

Fig. 1. Standard oxidation-reduction potentials of reducers specified in Table 6. 1 − basic reaction: $MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$, other labels correspond to numbers of the verses in Table 6. The figure comprises conventional group of reducers, in the sequence of descending potential: sulphuric reducers, organic acids, alcohols (−OH groups). The colors correspond to temperatures: 25 °C, 55 °C, 85 °C.

batteries, lithium, cadmium and nickel−cadmium batteries) are separated from the stream of spent batteries. Zinc−carbon and zinc−manganese batteries after sorting are directed for further mechanical processing. They are crushed and ground, and subsequently undergo magnetic separation. These operations result in three fractions: ferromagnetic (referred to as "scrap iron", the composition of which is based on such metals as iron, chromium and nickel), diamagnetic (referred to as "alternative fuel", in which plastics, paper and tar are gathered), and paramagnetic containing other metals (manganese and zinc in particular) and graphite.

5.2. Paramagnetic fraction

The paramagnetic fraction derived from mechanical processing of battery wastes is not homogeneous. It is composed of the so called "black mass" (powders of metals, graphite, electrolyte components, crushed construction materials), in which large pieces of polymer battery containers can be found, as well as various types of polymer spacers, pieces of paper and boards, wool sealing the spaces inside the battery, various sizes of broken graphite electrodes and metal elements of casings. Due to such non-homogeneity of the material supplied for studies, it required additional fractioning. It was performed by sieving 1 kg of the original material through a set of sieves, isolating three fractions of grain sizes: (1)≥5 mm, (2)≤2 ≤ 5 mm and (3)≤2 mm. The mass share of these fractions is presented in Table 7.

In the "black mass" the ø ≤ 2 mm fraction is predominating. Furthermore, presence of larger fragments of metallic, polymer fragments, paper and broken electrodes after mechanical processing was observed in 5 ≤ ø > 2 and ø ≥ 5 mm fractions. Therefore, the ø ≤ 2 mm fraction was selected for further studies. The content of zinc and manganese as well as other accompanying metals in this fraction is presented in Table 8.

Table 7
Share of grain fractions in the original paramagnetic material delivered from industrial processing of battery waste, weight %.

Paramagnetic fraction, % wt.		
≥ø 5 mm	5 mm ≤ ø ≤ 2 mm	ø ≤ 2 mm
13.5	8.0	78.5

Table 8
Content of metals in the $\varnothing \leq 2$ mm paramagnetic fraction, g kg^{-1}.

Metal content	Metals										
	Zn	Mn	Fe	Ni	Cd	Cu	Hg	K	Na	Co	Cr
[g kg^{-1}]	22.8	21.0	0.850	0.260	0.640	0.0170	0.0110	1.49	0.170	0.0320	0.007

5.3. Acidic leaching of $\varnothing \leq 2$ mm paramagnetic fractions with addition of reducers

Three substances specified in Table 6, i.e. H$_2$O$_2$, urea and oxalic acid were selected as reducers for leaching trials. Hydrogen peroxide was successfully used for multiple times in the leaching of battery wastes (Table 4), oxalic acid was mentioned only in one work (also Table 4, with moderate success) whereas the use of urea as a reducer was not mentioned. Unwashed $\varnothing \leq 2$ mm paramagnetic fraction was soaked with distilled water (120 cm^3) and leached with 95% sulphuric(VI) acid, added in an amount estimated as necessary for leaching of zinc and manganese plus amount necessary to balance H$^+$ ions of the appropriate reduction reaction (Table 6) with a small excess (which totally corresponds to 0.156 mol of H$_2$SO$_4$ for 20 g of the battery paramagnetic fraction). After addition of the sulphuric acid the following reagents were added: perhydrol (H$_2$O$_2$ — analytically pure, 30%), urea (CO(NH$_2$)$_2$ — analytically pure, 99%) or oxalic acid (etadien acid, C$_2$H$_2$O$_4 \cdot$2H$_2$O — analytically pure, 99.8%). Due to the fact that a part of the manganese was extracted to a solution without the use of a reducer (what was established in separate trials, Table 10 — 31.5%), the amount of the added reducer was calculated as 125% of the stoichiometric demand (according to the reactions specified in Table 6) in relation to the amount of manganese not activated in the leaching without the addition of a reducer. In case of the urea, it was finally used in large excess (due to the lack of reaction). The leaching parameters are specified in Table 9.

The procedure for leaching included: (1) weighing 20 g of the substrate and transferring it into a beaker of a capacity of 250 cm^3, (2) soaking with distilled water in the amount of 120 cm^3 (these proportions are defined further as s/l — the ratio of the solid phase to the liquid phase: 1/6), (3) adding 16 g of 95% sulphuric(VI) acid to the suspension as well as an appropriate amount of the reducer (Table 9), (4) leaching for 1 h with mixing of the suspension with a magnetic stirrer with the speed of 200 rotations per minute, (5) adding the reducer at the beginning of leaching, after 30 min or after 45 min. After completion of leaching, solution was separated from the solid phase by filtration under low pressure. The residue after leaching (i.e. filter cake) was washed with 200 cm^3 of hot water and the mixture was stirred by another 30 min. After 24 h, the solution was separated from the solid residue again by filtration under low pressure. The sludge was dried in the temperature of 105 °C for 24 h and weighed. The contents of metal in the solutions were determined with atomic absorption spectroscopy (GBC Avanta apparatus).
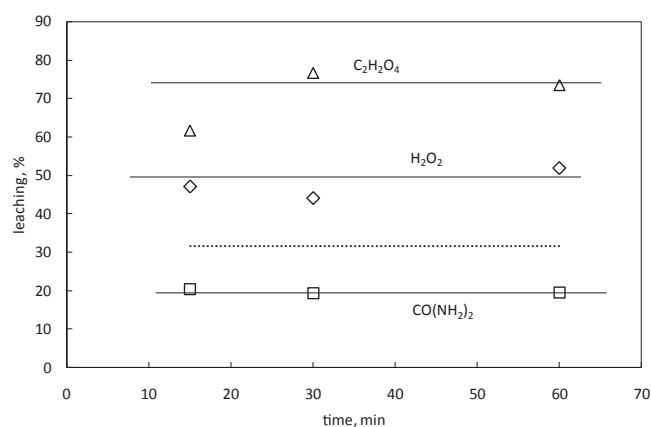
6. Results and discussion

The level of leaching of manganese in the function of addition of reducers (C$_2$H$_2$O$_4$, H$_2$O$_2$, CO(NH$_2$)$_2$) and time of reduction (15, 30,

Table 9
Parameters of leaching with sulphuric(VI) acid of a crude $\varnothing \leq 2$ mm paramagnetic fraction. t — time, mp — mass of the sample, n — moles of the sulphuric acid and reducers.

Reducer	t, [min]	$m_{p,}$[g]	$V_{H_2O,[cm^3]}$	$n_{H_2SO_4,[mol]}$	$n_{reducer}$[mol]
H$_2$O$_2$	60	20	120	0.156	0.065
CO(NH$_2$)$_2$					0.19
C$_2$H$_2$O$_4$					0.066

Table 10
Level of manganese leaching in a function of reducer additions and the reduction time, in % (leaching parameters are specified in the text).

Reducer	Leaching solution	Washing solution	Total in both solutions
Time of reduction 15 min			
H$_2$O$_2$	42.6	4.57	47.1
CO(NH$_2$)$_2$	19.0	1.38	20.4
C$_2$H$_2$O$_4$	57.1	4.44	61.6
Time of reduction 30 min			
H$_2$O$_2$	38.5	5.58	44.1
CO(NH$_2$)$_2$	18.5	0.74	19.3
C$_2$H$_2$O$_4$	65.6	11.1	76.7
Time of reduction 60 min			
H$_2$O$_2$	47.5	4.40	51.9
CO(NH$_2$)$_2$	18.2	1.25	19.5
C$_2$H$_2$O$_4$	68.1	5.42	73.5
Trial without the reducer	26.6	4.44	31.5

45 min) is specified in Table 10. These results are also presented graphically on Fig. 2. With reference to the obtained results for the selected reducers, the oxalic acid is the most effective reagent, although with the time of reduction no shorter than 30 min. In this case 74–77% of manganese leaching is obtained. This result is in accordance with the one specified in Table 4 (70% in the time of 5 h of leaching in a temperature of 80 °C). On the other hand, manganese leaching with hydrogen peroxide did not depend on the time of the process and oscillated around 50%. This result should be compared with the data from Table 4. They suggest that the level of transition of manganese into a solution was very variable in the literature studies and was oscillating between 30% and 100%. What is worth to note is the fact that this variety is hard to correlate with the leaching parameters specified in Table 4, however the present conditions of the process and the obtained result matches with similar conditions and the result obtained by Bartolozzi M. et al. [46]. The urea (CO(NH$_2$)$_2$) had almost no effect on the manganese recovery. When this compound was added to the solution, the level

Fig. 2. Level of manganese leaching in a function of reduction time: 15, 30, 60 min, %. The dotted line indicates the level of manganese leaching in a 60 min trial without addition of the reducer.

of manganese leaching decreased from approximately 30% for the reference process (leaching in identical conditions without the addition of the reducer) to approximately 20%. It is interesting that the proportional decrease of transition of the manganese into solution also concerns washing off of the sludge after the process of leaching. This may be related to a proportional decreasing of concentration of this element in the original leaching solution (therefore retention in the sludge). The inhibiting role of the urea in the process of manganese leaching - which is inconsistent with the data of Table 6 — cannot be explained without additional studies.

Variations of the temperature of the process are very characteristic. In each case, after addition of sulphuric acid into suspension of battery substrate, the temperature increased to 46–48 °C. Next, it gradually decreased to approximately 32–34 °C in the reference trials (without the addition of the reducer). The effect of adding the reducer on the solution temperature was different. In the case of urea, practically no changes in relation to reference trials have been observed. The addition of H_2O_2 resulted in a slight increase of the temperature (approx. 1 °C) whereas the addition of $C_2H_2O_4$ resulted in a significant increase of the solution temperature (approx. 5 °C). These effects were even more evident if reducer was added at the beginning of the process, that is at higher temperature (addition of oxalic acid in the first minute resulted in the increase of temperature of the solution by 6–7 °C after 10 min, the increase of temperature after the addition of hydrogen peroxide was minimal). These effects are clearly correlated with the level of manganese leaching and, taking into account the dependencies presented on Fig. 2, they are probably the result of the leaching reaction.

7. Summary

The analysis of oxidation-reduction potentials of reactions coupled with the reaction of reduction of MnO_2 to Mn^{2+} allows, from the thermodynamic point of view, for specification of their sequence taking into account reagent activities and pH of the solution. However, position of the reducer in these sequence of potentials does not guarantee the efficiency of the reduction reaction. It seems rather that kinetic parameters and reaction mechanism are equally important. The best results of leaching were obtained by the use of reducer with a lowest potential (oxalic acid). The reducer with a potential in the middle of the scale (urea) appeared to be entirely ineffective. Also, the reducer the most frequently discussed in the literature as a factor supporting the leaching process, i.e. hydrogen peroxide (located in the upper part of the potential scale) was merely effective. On the other hand, it seems that chloride ions, mentioned in literature as a potential reducer [53], shall not be effective, particularly in not very acidic environments and in low temperatures. Finally economical study on cost connected with use of reducer that gave best results (oxalic acid) and most popular one (hydrogen peroxide). Basing on current market prices [54] of oxalic acid and hydrogen peroxide (30% sol.) which are 550$/MT, 300$/MT respectively and results of leaching achieved for mentioned reducers (Table 10), conclusion is that although hydrogen peroxide is cheaper than oxalic acid, overall process is about 25% cheaper when performed with oxalic acid.

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